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# THE TECHNOLOGY OF THE COTTONSEED CRUSHING INDUSTRY

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Cottonseed constitutes the principal co- or by-product of cotton production and normally returns to the farmer from 100 to 200 million dollars annually.

The value of cottonseed and, hence, the price received for it by the farmer, depends on the value of its derived products which consist of linters, oil, meal, hulls, hull fiber, and hull bran. The price received for each of these derived products in turn depends on the uses and applications which they enjoy. This dependency of values can be traced from the seed to the finished product, be it shortening derived from the oil or lacquer derived from the linters.

The cost of conversion of one crude, intermediate or semi-finished product, to a more highly refined or finished product, is inextricably involved in and is of prime importance to the price received or paid for any given derived product. This cost of cenversion depends on many factory which may be divided for purposes of discussion into two broad classes, namely, economic and technologic. Some of the economic factors have been set forth and discussed by Mr. John F. Moloney under the title, "Cottonseed Oil: A Typical American Industry." Some of the technologic factors will be discussed here.

The technologic factors include the skill and ingenuity of the processor, the efficiency of the equipment employed, the power and labor involved, and most important of all, the state of development of the processes employed.

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Although the early history of the origin of the commercial extraction of oil from cottonseed is somewhat confused, it would appear that the process is a truly American contribution to agricultural industry. The period from 1800 to 1850 was largely experimental, both as regards process and equipment, and in 1865 there were but seven cottonseed oil mills in the United States. These were further increased to 26 by 1870, 119 in 1890, and 357 in 1900. During the 1916-17 season, 763 mills were engaged in crushing cottonseed but since then the number of active mills has shown a steady decline to about 460 in the 1939-40 season.

More officient delintering machines were introduced during the period 1870-90. Between 1890 and 1900, the hydraulic press was introduced and improved methods of cooking meats were developed. The continuous screw press was introduced shortly after the turn of the century, but its adoption by the cottonsced crushing industry was not rapid. Although a considerable number of continuous presses are now in use in the cottonseed industry, the bulk of the crop is still processed in hydraulic presses.

During the first quarter of the twentieth century, other improvements were made in the vegetable oil industry, especially in refinery operations, and in 1910 catalytic hydrogenation was applied to the hardening of cottonseed oil. Progress since then, and until quite recently, has been principally along the lines of improvements in existing equipment and processes in order to increase their capacity and efficiency.

Recent activity, both in industrial research laboratories and pilot plants, has been directed toward the possibilities of developing continuous processes in the oil mill and refinery, as well as in the related utilization industries. Considerable effort is being directed toward the development of processes which represent radical departures from present practices and

cquipment, as for example, solvent extraction of seed, physical methods of refining, and continuous methods of deodorizing the oil. The experimental work on the development of improved processes is being accompanied by intensive efforts to improve the quality of existing products and to develop new products having modified properties and adapted to new uses.

The nature and trend of the above-mentioned developments will be reviewed here, and an effort will be made to evaluate them and their probable effect on the cottonseed oil and related industries.

# Cottonseed Oil Extraction

The various steps in the preparation and processing of cottonseed by the hydraulic method are too well known to require a very detailed description (3). Briefly, however, the process consists of a cleaning operation during the course of which the seed is passed over screens to remove sand, dirt, bolls, and stems, then under magnets to remove ferrous metals, followed by an air separation of leaf-trash and dust. After cleaning, the seed is delintered in one or two stages by passage through delintering machines which are similar in construction to gin stands. The seed is then cracked and the meats and hulls are separated by a combination of screening and air-flotation.

The residual meats are rolled into thin flakes averaging about 0.007 of an inch in thickness and cooked for 35 to 90 minutes in a steam-heated kettle at a temperature of about 235° F. From the cooker, the hot meats are molded with the application of slight pressure into thin cakes between hair wrappings. The wrapped cakes are then placed in hydraulic presses and subjected to a maximum pressure of approximately 4,000 pounds per square inch at the ram or 1,600 pounds per square inch at the cake. After drainage of the oil ceases, the residual cakes are removed from the press, trimmed, cracked and ground into meal.

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The processing of cottonseed as it is practiced in the hydraulic press room cannot be considered as highly efficient. Press room practice suffers much by comparison with most modern manufacturing processes which operate even on a fraction of the tonnage of the cottonseed industry.

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The hydraulic process is neither highly flexible in operation nor economical of power and labor, and lacks many of the advantages of a completely continuous operation. Some of these disadvantages are overcome by the use of the continuous press, of which several types are manufactured. These presses perform in a single machine, and in one continuous operation, all of the processes which are carried out in the typical cottonseed press room.

At least three different manufacturers market continuous presses of several sizes and models, all of which are more or less similar in principle, if not in actual design. These presses vary somewhat in capacity and efficiency and many of the largest types which are in operation in the soybean and other oilseed industries are capable of processing more than 20 tons of seed daily. In recent years a number of intermediate-size presses having capacities of the order of 14 tons of seed per day have been placed in operation in cottonseed oil mills.

Two of the three types of continuous presses which are currently in use in the United States are referred to as expellers and screw-presses, respectively, by their manufacturers. In both presses the seed is subjected to high temperatures and pressures of the order of 5 to 10 tons per square inch by being pressed between discontinuous helical projections of a shaft and a slotted cage or barrel made of heavy steel bars placed a few thousandths of an inch apart. Under the high temperature and pressure of the press, the seeds are ruptured, the protein becomes plastic, and the oil is squeezed out through the openings between the bars, while the meal emerges from the end of the bar-

rel.

The largest and latest type of expeller consists essentially of a series of three tempering chambers or troughs, a feed hopper, two barrels (one vertical and one horizontal), and a heat interchanger for cooling and recirculating the oil over the expeller barrel. In operation, the seed is continuously charged by means of a vertical feeder to the steam jacketed tempering troughs, where they are further heated to about 130° C. as they are moved along by a series of spiral conveyors. From the tempering trough, the seed is fed to the vertical barrel of the expeller proper from which the partially pressed seed passes to the horizontal barrel where the pressing operation is completed.

The separated oil flows out of the openings between the bars of the expeller cage, percolates through a coarse screen which removes the foots and collects in a reservoir at the bottom of the expeller.

Another make of continuous press which is currently marketed in the United States operates on the same principle and has approximately the same capacity as the expeller, but has smaller overall dimensions. The cottonseed is tempered in a single steam-heated trough and is then fed directly to the press. In passing through the barrel, the tempered seed is propelled first by a feeder screw and then by the main pressure worm, the feeder turning at twice the speed of the main shaft but having the same pitch. The two shafts are concentric and have separate thrust bearings located in the gear case at the feed end. The cake is discharged through an adjustable cone loaded orifice, while the oil flows from the drainage barrel and falls upon an endless revolving screen which separates most of the foots and returns them to the incoming stream of seed.

One continuous press accomplishes the same work that the rolls, cooker and several hydraulic presses can accomplish in the same time. The cost of press-cloths is eliminated, pressing conditions can be adjusted quickly and

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without interruption of operations, and relatively little labor is required because the operation is largely automatic.

Part of the rapid growth of the soybean oil industry in the past few years can be traced to the efficiency of the large-capacity (20 or more tons per day) continuous presses which are commonly used in that industry.

Although the hydraulic and continuous presses are capable, when properly operated, of producing good quality oil, and a cake which is well adapted to stock feeding, both methods result in incomplete recovery of the oil and more or less complete denaturation of the protein. The oil remaining in the press cake produced by either hydraulic or continuous pressing amounts to 5 to 7 percent on an equilibrium moisture basis and, as has been repeatedly pointed out, the residual oil which is sold for the price of meal represents an appreciable loss to the mill operator. If it were possible to reduce the 2 million tons of cottonseed meal which are produced annually from 6 percent to one percent oil content, an additional 200 million pounds of oil would be recovered. With a differential of 4 cents per pound between the price of oil and meal, the recovered oil would represent 8 million dollars in gross return to the oil mills. Should the practice of buying seed on an oil content basis become general, it will become increasingly important to recover the maximum amount possible. The denaturation of the protein as a result of the application of high temperatures and pressures renders it unfit for most industrial uses and, judging from some recent unpublished work, it would appear that it is even less valuable for feeding than the original unaltered protein.

Both of these disadvantages may be overcome by solvent extraction of the oil, which may be accomplished either by a batch or a continuous process. The oil content of the residual cake can readily be reduced to one percent, while the protein of the meal is only slightly affected by the processing.

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The meal, as well as the proteins which may be recovered from it, may therefore be adapted to other than feeding purposes and, as mentioned above, it may even be superior to ordinary press cake for feeding.

Solvent extraction of soybeans was successfully developed and applied in Europe on a large scale after the first World War and, in recent years, has been widely introduced into the United States. The total capacity of solvent extraction plants now in operation or under construction in the United States for the purpose of processing soybeans amounts to approximately 15 hundred tons or 50 thousand bushels per day. These plants operating on a 300-day basis can extract a total of 450 thousand tons or 15 million bushels of soybeans annually.

Dr. David Wesson, who for many years advocated the introduction of solvent extraction processes in the cottonseed industry, stated in 1930 that any acceptable solvent process must necessarily meet the following conditions:

- 1. Produce oil and meal free from the solvent.
- 2. Operate without too much supervision to produce uniform results throughout the season.
- 3. Be comparatively free from unusual fire hazard.
- 4. Recover a large portion of the solvents used.
- 5. Offer reliable, uninterrupted operation.

And further, in order to replace hydraulic or expeller press plants, the solvent process must:

- 1. Be simple and easily supervised.
- 2. Require a low first cost.
- 3. Produce an absolutely solvent-free oil.
- 4. Be safe.

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It can hardly be claimed that any solvent extraction process fulfills all of these requirements and especially those which Dr. Wesson probably considered most important, namely, simplicity in construction and operation, low first cost, and freedom from fire hazard. Nevertheless; the present rate of expansion of the solvent extraction process in the soybean industry in the United States would seem to contradict the statements of Wesson.

It cannot, however, be assumed that the application of solvent extraction to cottonseed could be accomplished with the same relative ease as has been the case with soybeans. As a matter of experience, no oil-bearing material has been processed by solvent extraction methods on a scale comparable with soybeans, although attempts have been made to adopt the same processes and equipment to cottonseed, linseed, peanuts, copra, fish scrap, garbage grease, spent distiller's grains and many other oleaginous materials.

With the exception of soybeans and spent distiller's grains, solvent extraction of oleaginous materials has been carried out in small batch units which offer little advantage and considerable disadvantage over mechanical methods, except for the more complete removal of oil.

The successful application of solvent extraction to soybeans is due in a considerable measure to the inherent nature of the seed. The structure and chemical composition of the soybean is such that it is readily amenable to flaking to produce particles thin enough to permit ready penetration of the solvent and, at the same time, strong enough to withstand fracturing and general disintegration during passage through the extractor.

One of the principal difficulties encountered in the extraction of linseed and cottonseed results from the solution of the intercellular binder during extraction with the consequent disintegration of the individual flakes. The large amount of finely divided material thus produced results in compacting of the solids, uneven extraction due to channeling, and ultimate clogging of the extractor.

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Many factors will require investigation before a successful continuous solvent extraction method can be developed for cottonseed. Such factors as the optimum particle size, time of contact between solvent and solid, ratio of solvent to solid, temporature, type of solvent, optimum moisture content of the seed for flaking and of the flakes for extraction are but a few of the more simple and more readily determinable factors which need investigation. The optimum conditions for the continuous recovery of the oil and solvent and the complete removal of solvent from the meal without degradation of the protein, the effect of subsequent processing on the oil and meal, and many other problems must be investigated before a successful continuous solvent extraction process for cottonseed can be developed.

Even after the purely technological problems of the process itself have been solved, other collateral problems will require solution. For example, the successful operations of solvent extractions for oil seeds is predicated on the efficiency of large units as compared with small or medium sized units. Furthermore, the cost of solvent extraction units is quite large, irrespective of size, and practically year-round operation is required. On the basis of present experience, units of 100 tons daily capacity constitute about the minimum size commensurate with good efficiency. Units of 300 tons daily capacity would be preferable and 400 tons or larger would provide the greatest over-all efficency and economy. Such units would be capable of extracting 90 to 120 thousand tons of cottonseed annually, if operated on a 300-day basis, which must be considered as a minimum operating period. In order to extract the average quantity of cottonseed processed annually for the 10-year period 1923-37 which amounted to 4,709 thousand tons, only 52 of the 300-ton units or 40 of the larger units would be required in contrast to the 551 mills and 2,731 presses which were engaged in crushing cottonseed 10 years ago.

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The introduction of large-scale solvent extraction plants and the consequent reduction in the total number of active mills would necessitate drawing seed from much greater distances in order to permit year-round operation. This change would in turn necessitate shipment of seed from distant points and the erection of large storage facilities at the processing plant. The problems of drying, transporting, and storage of seed would have to be considered and solved.

The successful storage of large volumes of seed and continuous processing would tend to eliminate much of the variation in cil and meal quality which now results from the processing of many individual batches of seed of varying composition and quality. The greater uniformity in quality of the crude oil thus produced would permit greater standardization of the refinery operations.

In the light of the above discussion, it is obvious that widespread introduction of large-scale solvent extraction cannot be expected for many years to come. In view of the estimated investment of 200 million dollars in present oil mills and the requirement of an investment of 50 million dollars to 100 million dollars in new capital to erect the necessary solvent extraction plants and accessory seed-storage facilities, it is evident that the development of solvent extraction in the cottonseed industry, should it ever be realized, will be gradual and extend over many, many years.

#### Refinery Operations

#### Refining:

Crude cottonseed oil as produced by the various pressing processes contains variable quantities of free fatty acids, coloring matter, phosphatides, albuminous or mucilaginous substances, aldehydic, ketonic, and other odorous constituents which render it unsuited for edible purposes. It is necessary, therefore, to subject the oil to various refining operations for the reduction, or

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more or less complete removal, of these objectionable components. The first step in the refining of crude. cottonseed oil consists in treating it with alkali for the purpose of neutralizing the free fatty acids. When destined for use as a salad or cooking oil, or for the production of mayonnaise and salad dressings. the oil must be further refined by bleaching, deodorization, and winterization. Until recently the neutralization operation was carried out by the so-called open-kettle method. In the past few years, continuous methods of neutralization and separation of the soap stock have been introduced into the industry, and at the present time, considerable experimental work is being carried out in an effort to develop so-called mechanical refining methods which avoid the use of alkalies. In the batch method of refining the neutralization is carried out by the addition of alkali to the oil contained in large open top cylindrical or rectangular tanks called refining kettles, which are equipped with variable speed controlled agitators, heating coils or steam jacket, sprays for introducing the alkali solution, and a jacketed settling cone. Refining kettles holding 60 to 100 thousand pounds of oil, are not uncommon. Although the exact details of the refining operation vary from plant to plant, in general the oil is maintained at about atmospheric temperature while it is treated with caustic soda in slight excess above that required to neutralize the free fatty acids. Heating is carried out with moderate stirring until the so-called "break" appears. The break consists of small particles of scap derived from the free fatty acids originally present in the crude oil, excess caustic soda, some unsaponifiable matter, and other impurities. With continued heating and slow stirring, the small particles coalesce and when a temperature of 65° to 70° C. is reached, they become fluid and tend to settle. Heating and stirring are discontinued at this point and the soap stock is permitted to settle below the neutral oil. After settling in the refining kettle for 12 to 24 hours, depending on the production capacity and schedule,

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the supernatant oil is drawn off. The neutralized oil is washed by stirring with water, after which it is again allowed to settle.

The batch process of neutralization has been superseded in recent years to a considerable extent by the so-called continuous centrifugal method. In the latter process crude oil is pumped to a feed tank equipped with an agitator to insure thorough mixing and to avoid the introduction of large quantities of settlings to the refining apparatus at any one time. Caustic soda solution of requisite strength is contained in a separate tank. Oil from the feed tank is withdrawn by a centrifugal pump and passed through a proportionometer adjusted to deliver the proper percentage of caustic soda. The oil and caustic soda, properly proportioned, leave the proportionometer by separate lines and are introduced into a high speed mixer. The resulting emulsion is forced through a tubular heater where the temperature is raised to  $60^{\circ}$  to  $65^{\circ}$  C. The time of contact between the oil and lye in the mixer is less than a minute and in the heater about 2 minutes, after which the oil and soap stock are continuously separated in a high speed continuous centrifuge.

The refined oil from the centrifuge is continuously washed and dried by the use of a combination of water and oil mixing tanks, centrifuges for the reseparation of the water, and vacuum dryers for the oil. This process, which is already highly developed and quite efficient, can no doubt be improved both with respect to the volume of oil processed per unit of installation and by further simplification of the several units which comprise the over-all process.

In addition to the two methods described above, several other methods are under investigation, especially in the United States, which have for their objective the refining of cottonseed as well as other vegetable oils by means of activated absorbents or by countercurrent scrubbing with solvents in packed towers. Two processes for the refining of vegetable oils by a continuous regen-

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erative process employing activated absorbents have been patented. One of these employs activated tricalcium phosphate and the other a hydrated aluminum silicate as the absorbing agent. Neither process has as yet been carried out on a commercial or even a pilot plant scale, but such work as has been reported indicates that the processes may possibly be employed successfully, although many of the details relative to the design and capacity of the equipment have yet to be worked out.

Countercurrent scrubbing of vegetable oils with a cold solvent such as alcohol has been used commercially in Europe for some years and a similar process may possibly be of value for the refining of cottonseed oil when the recovery of by-product sterols and similar components is desired.

It should also be mentioned that some work is being done in connection with the pre-refining of cottonseed and other vegetable oils. These prerefining processes have for their objective the removal of certain easily separated impurities such as gums, mucilaginous materials, and phosphatides prior to alkali refining. These operations are accomplished simply by treating the oil with wet steam or with dilute solutions of mild alkalies or alkaline salts, in order to hydrate and coagulate the phosphatides, gums, and other materials so that they may be separated from the oil by settling or contrifuging. This type of pre-treatment results in very low subsequent refining losses, as might be expected, and produces a high-quality finished oil. It also makes possible the recovery of phosphatides and other constituents carried out of the oil during the degumming operation.

#### Bleaching:

After the cottonseed oil is refined, washed and dried, whether by the batch or continuous method, it is bleached to remove most of the coloring matter. To accomplish this operation, the washed and dried oil is run into

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an open tank fitted with a heating coil and agitator. In some cases the operation is carried out under vacuum in a closed tank similarly equipped with heating coils and agitator. Bleaching may be accomplished by fuller's earth, acid-activated bleaching clays, or by mixtures of activated clay and activated carbon. The bleaching agents are usually added after the oil is brought to a temperature of  $75^{\circ}$  to  $90^{\circ}$  C. Heating and agitation are continued until the temperature reaches approximately  $110^{\circ}$  C. or higher, and these conditions are maintained for an interval of 15 to 30 minutes. At the end of the bleaching period, the mixture is punped through a filter press which retains the bleaching agent and absorbed materials. This process, as it is at present perfromed, is a batch operation.

During the past several years efforts have been made both in the laboratory and on a pilot plant scale to develop continuous heat and clay bleaching methods. One such process has already been carried out on a semi-plant scale, with the result that it has become evident that much more experimental work will be necessary before any large-scale installations can be considered likely of success.

Where small batches of many different types of oils must be handled, it is probable that a continuous method of bleaching may prove of little advantage because of the considerable hold-up and consequent necessity for flushing the system before the next batch of oil can be treated. However, in the case of those industrial concerns which handle large volumes of nearly identical oil for the production of a single finished product, a continuous countercurrent bleaching system would appear to offer considerable advantage.

# Winterization:

The process of winterization of cottonseed oil, which may be carried out prior or subsequent to deodorization, has always represented a bottleneck in the production of finished salad oils. As the process is normally carried out, the oil is cooled by one of several different methods of refrigeration for a period of about 5 days, during which time the so-called stearine crystalizes from the liquid glyceride fractions. After separation of the solid material is complete, the mixture is pumped by means of air pressure through filter presses to separate the solid crystalline material from the liquid portion.

The process is not only time-consuming, but it requires a considerable portion of the total storage capacity of the plant and results in large intraplant inventories for considerable lengths of time. There is no reason, at least theoretically, why this process cannot be speeded up by the application of a similar type of process which is employed for the dewaxing of petroleum oil. Such a method would require that the oil be dissolved in a suitable solvent, cooled rapidly to a moderately low temperature, and the solid material continuously separated by centrifuging or filtration. The residual oilsolvent mixture would then have to be separated by distillation or some other suitable means. The crystallization, separation of the solvents, and recovery of the oil could all be made continuous and carried out in a matter of minutes or hours instead of days, as is the case at present. An installation for performing these operations should not require a great deal of space in a refinery and should be simply and economically operated, provided the proper types of solvent and equipment are selected.

# Deodorization:

Following the various treatments of neutralization, washing, bleaching, and winterizing, cottonseed oil still retains a characteristic taste and odor which is imparted to it by substances of low volatility. The removal of these substances is effected in the final step of the purification process.

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Deodorization is generally carried out by the batch method, although in the past two or three years a number of continuous deodorizers have been installed in various refineries. The total capacity of the continuous deodorizers which have been installed to date amounts to approximately 20 thousand pounds per hour or 140 million pounds per 300-day year.

Various designs of batch deodorizers are in use and, although differing somewhat in construction details, they consist essentially of cylindrical vessels of approximately 20 thousand pounds capacity which are provided with a system of baffles to prevent carrying over the oil with the steam. Accessory equipment usually consists of a multiple stage steam-jet vacuum pump, steam compressor or other means of superheating the steam, a thermo-compressor to compress the vapors from the deodorizer, and a barometric condenser. The steam enters the bottom of the column of cil 8 feet or more in height and passes upward and out through the condensing system. Temperatures of 180° to 210° C. and a vacuum of 5 to 12 mm. for 6 to 8 hours or longer are required to complete the deodorization.

No fixed conditions of deodorization can be set for all types of cottonseed oils, and the proper temperature, flow of steam through the oil, and length of time of deodorization commensurate with the production of the highest quality in the finished product depend on the oil and the skill and past experience of the operator. When, in the judgment of the operator, the oil has been properly deodorized, it is dropped to a vacuum tank equipped with cooling coils where it is cooled before opening it to the atmosphere.

The disadvantages of the batch system of deodorization are the length of time the oil must be heated, the poor contact between the oil and steam, and the hydrostatic pressure which increases from the surface to the bottom of the oil layer. Since 17 inches of cottonseed oil are equivalent to 1 inch of

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mercury, the pressure at the bottom of an 8-foot column of oil under a pressure of 0.25 inch at the surface amounts to 5.25 inches.

A number of continuous deodorizers have been developed in the United States and in Europe which eliminate most of the disadvantages of the batch deodorizer. The systems are all somewhat similar in principle and depend for their action on flowing a thin film of preheated oil down and over bubbling caps or plates against a rising current of superheated steam. Deodorization of the oil is carried out in a high vacuum in 4 to 6 minutes, following which the oil is rapidly cooled by circulation through cooling coils. In addition to the advantages of continuous operation, a product of high quality is obtained with a smaller expenditure for heat and an over-all operating cost approximately one-third that of the batch deodorization method.

The rate at which continuous deodorizers have been installed in the past two years and the satisfactory service and economies which have accompanied them clearly indicate that the development is a permanent one and it may be expected that an increasing volume of oil will be treated by this method.

#### Hydrogenation

The application by Norman in 1903 of catalytic hydrogenation to animal and vegetable fats and oils in order to convert them from liquids to solids, opened a new outlet for cottonseed oil which has grown to be of first importance to this industry. The consumption of one billion pounds annually of cottonseed oil in the shortening and oleomargarine industry has been made possible through the application of science and technology to the development of the hydrogenation process. From 1910 onward many improvements have been made in the industrial hydrogenation of cottonseed oil.

The development of the nickel catalysts and suitable supports, the large scale production and purification of hydrogen, the determination of

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optimum temperatures and pressures of the various hydrogenation reactions, and at least a partial understanding of the reaction mechanism have contributed to the successful industrial development of the hydrogenation of cottonseed oil. However, it must be admitted that, after 40 years of research, the course of the hydrogenation reactions with fatty acid glycerides is incompletely understood and the process is still operated more or less enpirically.

One of the unsolved problems of the cottonseed oil-hydrogenation process is the lack of adequate control of the isomerization reactions which accompany the hydrogenation. When cleic acid or a glyceride containing this acid is hydrogenated, it is transformed into stearic acid but, at the same time, part of the acid is isomerized to form a solid unsaturated acid having a lower melting point than stearic acid. The proportion in which this isomer is formed depends on the conditions of the reactions, including the temperature, pressure, and activity of the catalyst, the intimacy of the admixture of oil, catalyst and hydrogen, the rapidity of desorption of the reacting molecules of the catalyst, and perhaps still other factors.

Of these factors, the effect of the catalyst is especially marked, as indicated by the decreasing degree of isomerism induced by certain metal catalysts. The amount of isomerism decreases with the following catalysts in the order named: platinum, palladium, nickel, copper. It is quite likely that, if hydrogenation could be carried out in the absence of a catalyst, isomerization could be reduced markedly or entirely avoided. At first sight, hydrogenation without a catalyst may appear to be impossible or impractical, but at least one process has been suggested by which it might be accomplished.

When the hydrogenation involves a doubly unsaturated acid, such as linoleic acid or its glycerides, the reaction is more complicated, since the possibilities of reaction are more numerous. In practice, one of the double

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bonds reacts first, followed by saturation of the second bond, but at least two isomers are formed in the first stage of the reaction and two additional isomers in the second stage.

Apparently the selectivity of the hydrogenation can be controlled within limits and much research is at present in progress to determine the nature of the conditions necessary to produce a desired end product. The desirability of such control follows from the fact that the properties of the end product of the hydrogenation process are dependent upon the properties of the individual products of the mixture. Selective hydrogenation of cottonseed oil is, therefore, extremely important to the manufacturer of shortening and oleomargarine, as well as to producers of other types of hydrogenated fats and oils intended for non-edible consumption. It is also important, because of the objection on the part of certain consumers, for real or imaginary reasons, to the presence of solid isomers in some types of finished products.

The development of more rational control of the hydrogenation process is dependent on a knowledge of thermodynamic properites of pure fatty acids and glycerides of known structure. Data which are especially needed for this purpose pertain to the heats of combustion and heats of hydrogenation of pure synthetic glycerides.

Some data on the heats of catalytic hydrogenation of peanut oil have been recorded by Holmboe (2) and recently C. G. King and co-workers at the University of Pittsburgh have published results on the heats of combustion of pure synthetic glycerides. They have shown a marked difference in the relative stability of the alpha and beta monoglycerides and have calculated the energy of rearrangement of the beta isomer to be of the order of 9 thousand calories per mol. This value is quite high and may indicate the presence of

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an association complex in the alpha position. Much more data of this type, and especially of the various stereo-isomers of oleic and linoleic acid, are needed as a basis for the selective control of the hydrogenation process.

At the present time, considerable attention is being given to the possibility of continuous hydrogenation. Several such processes have been developed both in Europe and Asia. At least one of these processes has been carried through the pilot plant stage and a small commercial unit is now in operation in England. The introduction of continuous hydrogenation has led to the use of nickel oxide as catalyst, supported by the nickel itself, in the form of perforated plates or leaves. In the continuous method, the oil is in contact with the catalyst and hydrogen for a short time only and final refining is unnecessary. Furthermore, the oil leaves the reaction tubes with less than 1 part in 10 thousand of nickel and, consequently, it does not require filtration. (1)

The continuous process of hydrogenation is barely in its infancy, and in this country it has not received the attention which it deserves or which it has received abroad.

European workers, and especially Russian scientists, have been actively investigating the possibility of catalytic hydrogenation without the use of gaseous hydrogen. The method employs the principle of hydrogenationdehydrogenation of a hydrogen donor-oil system such as ethanol-cottonseed oil.

The dehydrogenation of stearic acid to produce unsaturated acids and glycerides has been experimentally carried out at high temperature in the presence of a catalyst and a hydrogen acceptor such as ethylene.

Oleic and saturated acids have been reduced by catalytic hydrogenation to the corresponding alcohols which in turn have been sulfonated to produce detergents, wetting agents and similar surface active materials.

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Much work is in progress and more is planned which should lead to an extension of knowledge of reactions involved, as well as to new processes and products of the hydrogenation industry. The results of this research are bound to have a marked influence on the consumption and use of cottonseed as well as other vegetable oils.

#### Summary

In the above somewhat cursory review of the technological developments which are in progress, or which are on the horizon of the vegetable oil industry, an effort has been made to point out their trend and possible effect on the cottonseed oil industry.

In conclusion it may be said that the cottonseed milling industry, which is now three-quarters of a century old, made rapid strides during the first half of this period after which it became relatively static. The lack of effective domestic competition with other sources of fats and oils no doubt created a false sense of security and tended to discourage research and development of more efficient processing methods.

Under the recent stimulus of competition from the domestic production of soybeans, the loss of export markets for cottonseed oil and lard, as well as the reduction in the supply of cottonseed resulting from the curtailment of cotton production, the cottonseed milling industry is now becoming interested in more efficient processing methods and in the general improvement of the products and by-products which it produces.

In the refining and utilization industries, a definite trend is observable toward the introduction of continuous methods and better integration of the various processing steps. Considerable attention is being devoted toward the possible recovery of byproducts and the development of new products having characteristics and properties adaptable to technical non-food uses.

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The tendency to look to research for the solution of the present problems confronting the cottonseed oil industry is in keeping with the general trend of industry as a whole, and it may be confidently expected that much benefit may be derived therefrom.

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# Literature Cited.

- (1) Armstrong, E. F. and Williams, K. A. Chim. Ind. <u>42</u>, 234 (1939); Chem. Age <u>41</u>, 271, 285 (1939); Chem. Ind. <u>59</u>, 5 (1940).
- (2) Holmboe, C. F., Ber. 71B, 532-41 (1938).
- (3) Woolrich, W. R. and Carpenter, E. L. Mechanical Processing of Cottonsced. Univ. Tenn. Eng. Expt. Sta. (1935).

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